

(9) P807305

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 May 2001 (31.05.2001)

PCT

(10) International Publication Number
WO 01/38861 A2

(51) International Patent Classification⁷: **G01N 23/00**

(21) International Application Number: **PCT/GB00/04452**

(22) International Filing Date:
23 November 2000 (23.11.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
9927555.4 23 November 1999 (23.11.1999) GB

(71) Applicant (*for all designated States except US*): **BEDE SCIENTIFIC INSTRUMENTS LTD [GB/GB]**; Bowburn South Industrial Estate, Bowburn DH6 5AD (GB).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **LOXLEY, Neil**

[GB/GB]; 9 Whitesmocks Avenue, Durham DH1 4HP (GB). **BOWEN, David, Keith [GB/US]**; Apartment 1002, 790 Washington Street, Denver, CO 80203 (US). **PINA, Ladislav [CZ/CZ]**; Janovska 373, 109 00 Prague 10 (CZ).

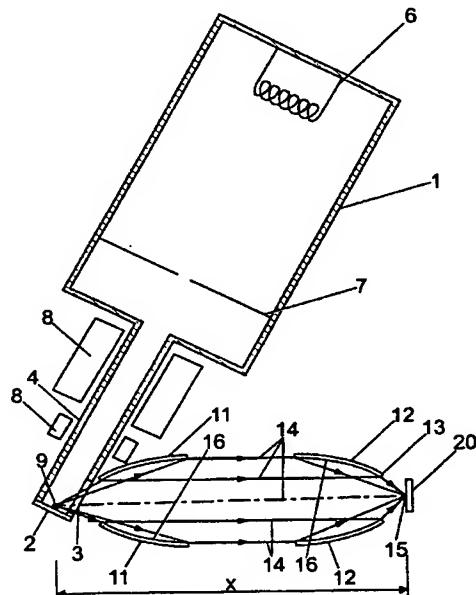
(74) Agent: **MURGITROYD & COMPANY**; 373 Scotland Street, Glasgow G5 8QA (GB).

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European

[Continued on next page]

(54) Title: X-RAY FLUORESCENCE APPARATUS



WO 01/38861 A2

(57) Abstract: This invention relates to a portable apparatus for carrying out X-ray fluorescence spectrometry on specimen materials at a distance from the apparatus. The apparatus comprises an X-ray generating tube (1), such as a microfocus tube, and two paraboloidal X-ray reflecting mirrors. The first collecting mirror (11) is positioned in close coupled arrangement adjacent the exit window (3) of the tube (1), such that it emits parallel X-ray radiation (14) to the second focusing mirror (12) which is aligned on the axis of and spaced apart from the first mirror (11). The second mirror (12) collects the parallel X-ray radiation (14) at its end closest to the first mirror (11) and emits X-ray radiation in a focused beam onto the specimen (20). The distance between the first and second mirrors is adjusted to suit the distance from the X-ray tube (1) to the specimen (20). Focal spots on the specimen (20) of diameter less than 15 µm are possible, enabling precise analysis of small areas of the specimen.



patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

- *Without international search report and to be republished upon receipt of that report.*

1 **X-ray Fluorescence Apparatus**

2

3 This invention relates to an apparatus and method for
4 carrying out X-ray fluorescence spectrometry (XRF),
5 and particularly to a portable apparatus which is
6 able to generate X-ray fluorescence in materials at a
7 distance from the apparatus.

8

9 X-ray fluorescence spectrometry is a non-destructive
10 technique for determining the elemental composition
11 of a wide variety of materials. X-ray fluorescence
12 (XRF) is the secondary emission of X-rays at
13 wavelengths characteristic of each element present
14 when a material is irradiated with a primary X-ray
15 beam. In commercially available XRF spectrometers
16 the bulk sample is usually irradiated directly by X-
17 rays from a sealed tube. The technique is
18 sufficiently sensitive to detect elements which are
19 present at concentrations as low as one or two parts
20 per million. There is however a requirement for

1 greater sensitivity in applications in which it is
2 desired to examine small areas on bulk samples or
3 where the sample itself is small. The type of
4 instrumentation required for this technique is
5 sometimes called Micro X-ray Fluorescence Analysis
6 (MXRFA or MXA) apparatus.

7

8 Several methods presently exist for MXRFA. Among
9 them is the use of mono-capillary and poly-capillary
10 X-ray focusing optics coupled to standard or
11 microfocus X-ray generating tubes. These suffer from
12 the drawback that samples have to be placed very
13 close to the output of the optic (generally less than
14 300 μm). The minimum focal spot generally
15 commercially available with polycapillaries is 28 μm .
16 This is relatively large and limits the fineness of
17 the resolution with which areas of a sample can be
18 analysed.

19

20 Another method which presently exists for MXRFA is to
21 use a synchrotron in conjunction with Fresnel lenses.
22 Such apparatus is massive and not portable, although
23 beams having a focal spot of only 1 μm can be
24 achieved, giving greater accuracy in analysis of
25 samples. This method suffers from the disadvantage
26 that synchrotron radiation sources are large fixed
27 facilities which are not portable and are not
28 available in most laboratories, so cannot be accessed
29 on a routine basis.

30

1 A further method of MXRFA which exists is the use of
2 a synchrotron in conjunction with mono-capillary
3 lenses. Such apparatus is also not portable, and
4 beam sizes are limited to a focal spot of 5-10 µm.

5

6 It is therefore an object of the invention to provide
7 an apparatus for carrying out X-ray fluorescence
8 spectrometry which is portable yet which is capable
9 of analysing samples of are less than 30 µm.

10

11 According to a first aspect of the present invention
12 there is provided an apparatus for carrying out X-ray
13 fluorescence spectrometry comprising an X-ray
14 generating tube and two paraboloidal X-ray reflecting
15 mirrors, the generating tube having an X-ray source
16 and an X-ray exit window through which X-ray
17 radiation from said source is emitted,
18 the first mirror being aligned on a first axis and
19 positioned in close coupled arrangement adjacent to
20 the exit window, the second mirror being aligned on
21 said first axis and being positioned in spaced apart
22 relationship to the first mirror,
23 the first mirror being adapted to collect diverging
24 X-ray radiation at its first end adjacent to the
25 collecting window and to emit X-ray radiation in a
26 substantially parallel beam at its second end,
27 the second mirror being adapted to collect
28 substantially parallel X-ray radiation at its first
29 end closest to the first mirror and to emit X-ray
30 radiation in a focused beam at its second end.

31

1 By using first and second mirrors in this way, the
2 focal spot on the target of the X-ray tube is
3 transferred to the image plane, at unity
4 magnification. The focal spot at the image plane on
5 the sample subjected to fluorescence has a high
6 brightness, and focal spots on the sample of diameter
7 less than 15 µm are possible.

8

9 Preferably the first and second mirrors are
10 cylindrical specularly reflecting mirrors.
11 Preferably the first end of the first mirror is
12 positioned between 5 and 50 mm from the X-ray source.

13

14 Preferably the apparatus further comprises a housing
15 containing the first and second mirrors.

16

17 The second mirror may be fixed in position relative
18 to the first mirror.

19

20 Alternatively the second mirror may be movable in
21 position relative to the first mirror. The apparatus
22 may further comprise a guide means for guiding said
23 second mirror in a direction parallel to the first
24 axis, and adjustment means for adjusting the spacing
25 of the first and second mirrors.

26

27 The apparatus may further comprise angular adjustment
28 means adapted to allow angular adjustment of the
29 mirror housing with the X-ray generator tube.

30

1 Preferably the X-ray generator tube is adapted to
2 produce an X-ray source at the target having a
3 maximum width of less than 50 µm, more preferably
4 less than 15 µm.

5

6 According to a second aspect of the present invention
7 there is provided a method of delivering X-ray
8 radiation to a specimen for the purpose of X-ray
9 fluorescence spectrometry using an X-ray generating
10 tube, the generating tube having an X-ray exit window
11 through which X-ray radiation is emitted,
12 the method comprising placing first and second
13 paraboloidal X-ray reflecting mirrors between the
14 exit window and the specimen,
15 using the first mirror to collect diverging X-ray
16 radiation at its first end adjacent to the exit
17 window and to emit X-ray radiation in a substantially
18 parallel beam at its second end,
19 and using the second mirror to collect substantially
20 parallel X-ray radiation at its first end closest to
21 the first mirror and to emit X-ray radiation at its
22 second end to a focused spot on the specimen.

23

24 Preferably the method uses an apparatus according to
25 the first aspect of the invention.

26

27 Embodiments of the invention will now be described,
28 by way of example only, with reference to the
29 accompanying figures, where:

30

1 Fig. 1 is a schematic view of two X-ray focusing
2 mirrors used in accordance with the invention to
3 focus an X-ray beam from the source on the X-ray
4 target to the sample to be subject to X-ray
5 fluorescence spectrometry;

6

7 Fig. 2 is a schematic view of an apparatus according
8 to a first aspect of the invention having mirrors
9 fixed relative to each other; and

10

11 Fig. 3 is a schematic view of an apparatus according
12 to a second aspect of the invention having mirrors
13 adjustable relative to each other.

14

15 Referring to Fig. 1 there is shown, in a schematic
16 form and not to scale, an X-ray generating tube 1
17 having an exit window 3, an electron source 6, an
18 anode 7, focusing and stigmator coils 8 and a target
19 2 on which is formed an X-ray source 9. A suitable
20 X-ray generating tube is the MICRO SOURCE™ tube
21 described in International Patent Application No
22 PCT/GB97/02022, which is a compact X-ray generator
23 capable of producing small-size, high intensity X-ray
24 sources for low power input. Typically the exit
25 window 3 of the generator 1 is provided in the narrow
26 portion 4 of the X-ray tube about which the X-ray
27 focusing coils 8 are arranged, to the side of the X-
28 ray target 2. A first X-ray focusing mirror 11, the
29 collection mirror, is positioned adjacent to the exit
30 window 3 in close coupled arrangement, and a second
31 X-ray focusing mirror 12, the focusing mirror, is

1 arranged coaxially with the first X-ray focusing
2 mirror 11, to transfer the . Suitable mirrors 11, 12
3 are MICROMIRROR™ X-ray optics as supplied by Bede
4 Scientific Instruments Ltd. The mirrors are
5 cylindrical specularly reflecting mirrors. Each
6 mirror comprises a cylindrical body having an axially
7 symmetrical passage extending therethrough. There is
8 an aperture at each end of the body which
9 communicates with the passage. The reflecting
10 surface is on the inside of the long axis of the
11 cylinder and has a shape corresponding to a
12 paraboloid of revolution about the long axis of the
13 cylinder.

14

15 A paraboloidal profile produces an almost parallel,
16 essentially non-divergent beam 14. The interior
17 reflecting surface 16 is coated in an exceptionally
18 smooth coating of gold or similar in order to provide
19 specular reflectivity. Typically the mirror is made
20 of nickel and is of the order of 10 to 100 mm in
21 length, typically about 30 mm. The outside diameter
22 of the mirror is typically 6 mm. The internal
23 diameter is typically less than 4 mm. The entry
24 aperture is generally smaller than the exit aperture.

25

26 The two mirrors have an identical profile. The
27 source to first mirror distance is in the range 5 to
28 50 mm.

29

1 Typically the X-ray generator produces a sub-15 μm
2 spot source on a target of less than 10 mm diameter
3 at a power of up to 30 W.

4

5 The first mirror or paraboloidal optic 11 has a high
6 angle of collection and reflects X-rays into a
7 substantially parallel beam. In practice a beam of
8 divergence less than 40 arc seconds can be achieved.

9

10 The second mirror or paraboloidal optic 12 takes the
11 parallel beam and focuses it down to a spot 15 on the
12 specimen 20 of a size similar to that of the X-ray
13 source, typically a spot with a diameter of less than
14 15 μm .

15

16 The focus 15 of the second optic 12 is typically
17 about 10 to 20 mm away from the far end 13 of optic,
18 giving a much more convenient working distance than
19 is available from prior art XRF apparatus, such as
20 monocapillaries.

21

22 The distance between the two optics 11, 12 may be
23 continuously changed without affecting the focal spot
24 quality, thereby allowing a range of source to sample
25 distances X to be achieved. Typically distance X
26 will be 100 mm or more.

27

28 X-ray optics have very well defined profiles and low
29 surface roughness, and therefore work at very high
30 efficiency. By using paraboloidal mirrors the
31 apparatus of the invention achieves broad band

1 transmission of X-rays, with an efficiency close to
2 1, since only double reflection of the X-ray
3 radiation is required.

4

5 The invention achieves high X-ray brightness at the
6 focal plane on the target, with a focal spot diameter
7 of as low as 10 μm .

8

9 The apparatus of the invention is truly portable,
10 giving it applications in areas such as forgery
11 detection, which require the apparatus to be taken to
12 the specimen.

13

14 A parabolic surface will produce a parallel beam if
15 the source is placed at the focal point. Conversely
16 a focused beam will be brought to a focus when a
17 parabolic surface is illuminated with a parallel
18 beam. Therefore the method and apparatus of the
19 invention serves to transfer the image of the X-ray
20 spot from the target to the specimen. It should be
21 noted that the target may not be perpendicular to the
22 axis of the of the mirrors, so that the effective
23 dimension of the image on the target, when viewed
24 along the axis of the mirrors, is less than the
25 actual dimension on the target.

26

27 The focal spot size at the specimen is thus primarily
28 determined by the spot size on the target of the X-
29 ray tube. Since the first mirror produces a parallel
30 beam, the focal spot size at the specimen is, within
31 practical limits, independent of the distance of the

1 second mirror along the beam axis. Therefore the
2 second mirror can be placed at the required distance
3 from the first in order to suit the geometrical
4 requirements of the equipment.

5

6 Figs. 2 and 3 show two schematic arrangements for
7 housing the apparatus of the invention.

8

9 In the simplest case, shown in Fig. 2, the collector
10 and focusing mirrors 11, 12 are aligned with each
11 other and are fixed within a cylindrical housing 30.
12 The housing is aligned relative to the X-ray source
13 9, shown purely schematically in Figs. 2 and 3, on
14 the beam axis 32, either fixedly or adjustably. The
15 housing 30 may be subject to a partial or total
16 vacuum, to improve the efficiency of the mirrors and
17 reduce energy absorption as the X-rays pass through
18 the gas in the housing 30. It is to be understood
19 that in practice the source 9 is part of an X-ray
20 generating tube 1 (not shown in Figs. 2 and 3).

21

22 In use the housing 30 is placed adjacent to the X-ray
23 source, and a control mechanism 35 allows fine
24 adjustment of the position of the housing 30 in the
25 x, y and z directions so that the axis 32 of the
26 mirrors is accurately aligned with the X-ray source 9
27 and directed to the specimen 20. The control
28 mechanism 35 may comprise any suitable mechanisms
29 which permit fine translational adjustment, such as
30 lead screws or Vernier controls.

1 In the example of Fig. 3, each mirror 11, 12 is
2 provided with a separate housing 40, 41. The
3 housings 40, 41 may further be contained in an outer
4 housing, not shown, which may be partially or
5 completely evacuated. The apparatus allows alignment
6 of the second mirror 12 relative to the first mirror
7 11 and translation of the second mirror 12 along the
8 beam axis 43 by means of control mechanism 44.

9

10 Alignment of the whole mirror assembly relative to
11 the X-ray source 9 is possible by means of control
12 mechanism 45. Mechanisms 44 and 45 are similar to
13 mechanism 35 described with reference to Fig. 2, and
14 are not described further.

15

16 Although the invention has been described with
17 reference to a microfocus X-ray generator, the
18 invention can be used with any suitable X-ray
19 generator which is capable of producing a small
20 source of sufficient intensity.

21

22 The mirror housing 30, 40 may be attached to the X-
23 ray tube 1 or may be positioned independently.

24

25 These and other modifications and improvements can be
26 incorporated without departing from the scope of the
27 invention.

1 **CLAIMS**

2

3 1. An apparatus for carrying out X-ray fluorescence
4 spectrometry comprising an X-ray generating tube (1) and
5 two paraboloidal X-ray reflecting mirrors (11, 12), the
6 generating tube having an X-ray source (9) and an X-ray
7 exit window (3) through which X-ray radiation from said
8 source is emitted,
9 the first mirror (11) being aligned on a first axis (32,
10 43) and positioned in close coupled arrangement adjacent
11 to the exit window (3), the second mirror (12) being
12 aligned on said first axis and being positioned in spaced
13 apart relationship to the first mirror (11),
14 the first mirror (11) being adapted to collect diverging
15 X-ray radiation at its first end adjacent to the
16 collecting window (3) and to emit X-ray radiation in a
17 substantially parallel beam at its second end,
18 the second mirror (12) being adapted to collect
19 substantially parallel X-ray radiation at its first end
20 closest to the first mirror and to emit X-ray radiation
21 in a focused beam at its second end.

22

23 2. An apparatus according to Claim 1, wherein the first
24 and second mirrors (11, 12) are cylindrical specularly
25 reflecting mirrors.

26

27 3. An apparatus according to Claim 1 or 2, wherein the
28 first end of the first mirror (11) is positioned between
29 5 and 50 mm from the X-ray source (9).

30

31 4. An apparatus according to any preceding Claim,
32 wherein the apparatus further comprises a housing
33 containing the first and second mirrors.

1

2 5. An apparatus according to any preceding Claim,
3 wherein the second mirror is fixed in position relative
4 to the first mirror.

5

6 6. An apparatus according to any of Claims 1 to 4,
7 wherein the second mirror is movable in position relative
8 to the first mirror.

9

10 7. An apparatus according to Claim 6, further
11 comprising a guide means for guiding said second mirror
12 in a direction parallel to the first axis, and adjustment
13 means for adjusting the spacing of the first and second
14 mirrors.

15

16 8. An apparatus according to any preceding Claim,
17 further comprising angular adjustment means adapted to
18 allow angular adjustment of the mirror housing with the
19 X-ray generator tube.

20

21 9. An apparatus according to any preceding Claim,
22 wherein the X-ray generator tube is adapted to produce an
23 X-ray source at the target having a maximum width of less
24 than 50 μm , more preferably less than 15 μm .

25

26 10. An apparatus according to any preceding Claim,
27 wherein the apparatus is portable and the X-ray generator
28 is a microfocus generator.

29

30 11. A method of delivering X-ray radiation to a specimen
31 for the purpose of X-ray fluorescence spectrometry using
32 an X-ray generating tube, the generating tube having an

1 X-ray exit window through which X-ray radiation is
2 emitted,
3 the method comprising placing first and second
4 paraboloidal X-ray reflecting mirrors between the exit
5 window and the specimen,
6 using the first mirror to collect diverging X-ray
7 radiation at its first end adjacent to the exit window
8 and to emit X-ray radiation in a substantially parallel
9 beam at its second end,
10 and using the second mirror to collect substantially
11 parallel X-ray radiation at its first end closest to the
12 first mirror and to emit X-ray radiation at its second
13 end to a focused spot on the specimen.

14

15 12. A method according to Claim 11, wherein the first
16 and second mirrors (11, 12) are cylindrical specularly
17 reflecting mirrors.

18

19 13. A method according to Claim 11 or 12, wherein the
20 first end of the first mirror (11) is positioned between
21 5 and 50 mm from the X-ray source (9).

22

23 14. A method according to any one of Claims 11 to 13,
24 wherein the focused spot on the specimen has a maximum
25 dimension of 50 μm .

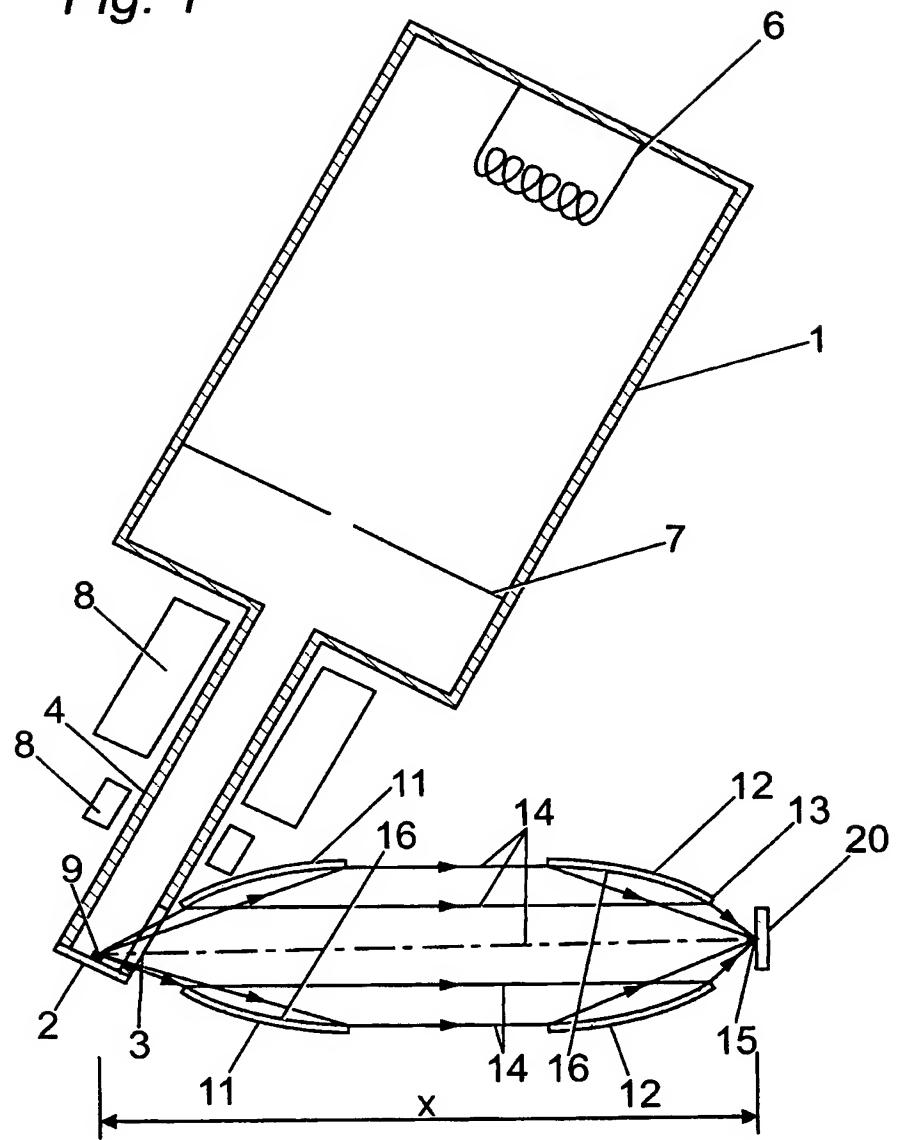
26

27 15. A method according to any one of Claims 11 to 14,
28 further comprising the step of adjusting the spacing of
29 the first and second mirrors to produce a focused spot on
30 the specimen.

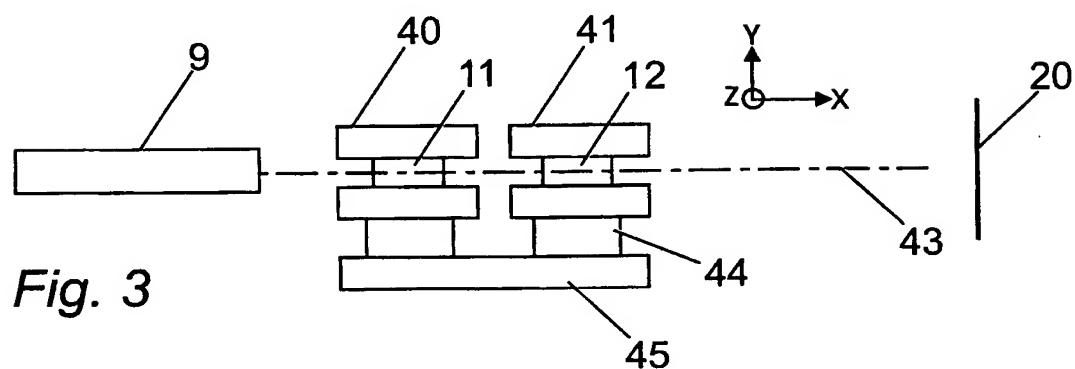
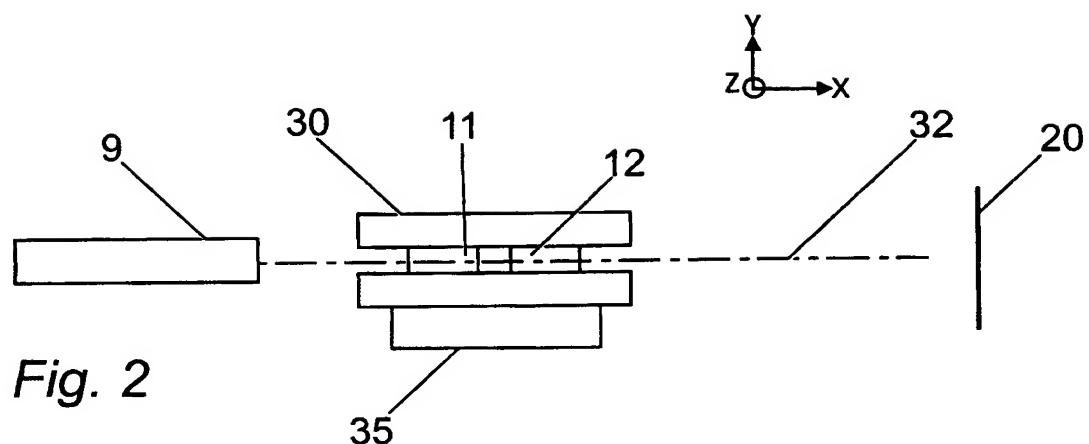
31

32 16. A method according to any one of Claims 11 to 15,
33 wherein the X-ray generator is a microfocus generator.

1 / 2

Fig. 1

2 / 2



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 May 2001 (31.05.2001)

PCT

(10) International Publication Number
WO 01/38861 A2

(51) International Patent Classification⁷: **G01N 23/00**

[GB/GB]; 9 Whitesmocks Avenue, Durham DH1 4HP (GB). BOWEN, David, Keith [GB/US]; Apartment 1002, 790 Washington Street, Denver, CO 80203 (US). PINA, Ladislav [CZ/CZ]; Janovska 373, 109 00 Prague 10 (CZ).

(21) International Application Number: **PCT/GB00/04452**

(74) Agent: **MURGITROYD & COMPANY**; 373 Scotland Street, Glasgow G5 8QA (GB).

(22) International Filing Date:
23 November 2000 (23.11.2000)

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(25) Filing Language: **English**

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European

(26) Publication Language: **English**

(30) Priority Data:
9927555.4 23 November 1999 (23.11.1999) GB

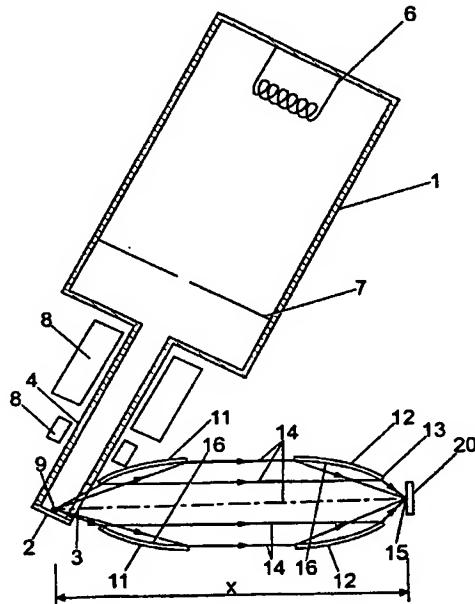
(71) Applicant (*for all designated States except US*): **BEDE SCIENTIFIC INSTRUMENTS LTD** [GB/GB]; Bowburn South Industrial Estate, Bowburn DH6 5AD (GB).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **LOXLEY, Neil**

[Continued on next page]

(54) Title: X-RAY FLUORESCENCE APPARATUS



WO 01/38861 A2

(57) Abstract: This invention relates to a portable apparatus for carrying out X-ray fluorescence spectrometry on specimen materials at a distance from the apparatus. The apparatus comprises an X-ray generating tube (1), such as a microfocus tube, and two paraboloidal X-ray reflecting mirrors. The first collecting mirror (11) is positioned in close coupled arrangement adjacent to the exit window (3) of the tube (1), such that it emits parallel X-ray radiation (14) to the second focusing mirror (12) which is aligned on the axis of and spaced apart from the first mirror (11). The second mirror (12) collects the parallel X-ray radiation (14) at its end closest to the first mirror (11) and emits X-ray radiation in a focused beam onto the specimen (20). The distance between the first and second mirrors is adjusted to suit the distance from the X-ray tube (1) to the specimen (20). Focal spots on the specimen (20) of diameter less than 15 µm are possible, enabling precise analysis of small areas of the specimen.



patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

- *Without international search report and to be republished upon receipt of that report.*

1 **X-ray Fluorescence Apparatus**

2

3 This invention relates to an apparatus and method for
4 carrying out X-ray fluorescence spectrometry (XRF),
5 and particularly to a portable apparatus which is
6 able to generate X-ray fluorescence in materials at a
7 distance from the apparatus.

8

9 X-ray fluorescence spectrometry is a non-destructive
10 technique for determining the elemental composition
11 of a wide variety of materials. X-ray fluorescence
12 (XRF) is the secondary emission of X-rays at
13 wavelengths characteristic of each element present
14 when a material is irradiated with a primary X-ray
15 beam. In commercially available XRF spectrometers
16 the bulk sample is usually irradiated directly by X-
17 rays from a sealed tube. The technique is
18 sufficiently sensitive to detect elements which are
19 present at concentrations as low as one or two parts
20 per million. There is however a requirement for

1 greater sensitivity in applications in which it is
2 desired to examine small areas on bulk samples or
3 where the sample itself is small. The type of
4 instrumentation required for this technique is
5 sometimes called Micro X-ray Fluorescence Analysis
6 (MXRFA or MXA) apparatus.

7

8 Several methods presently exist for MXRFA. Among
9 them is the use of mono-capillary and poly-capillary
10 X-ray focusing optics coupled to standard or
11 microfocus X-ray generating tubes. These suffer from
12 the drawback that samples have to be placed very
13 close to the output of the optic (generally less than
14 300 μm). The minimum focal spot generally
15 commercially available with polycapillaries is 28 μm .
16 This is relatively large and limits the fineness of
17 the resolution with which areas of a sample can be
18 analysed.

19

20 Another method which presently exists for MXRFA is to
21 use a synchrotron in conjunction with Fresnel lenses.
22 Such apparatus is massive and not portable, although
23 beams having a focal spot of only 1 μm can be
24 achieved, giving greater accuracy in analysis of
25 samples. This method suffers from the disadvantage
26 that synchrotron radiation sources are large fixed
27 facilities which are not portable and are not
28 available in most laboratories, so cannot be accessed
29 on a routine basis.

30

1 A further method of MXRFA which exists is the use of
2 a synchrotron in conjunction with mono-capillary
3 lenses. Such apparatus is also not portable, and
4 beam sizes are limited to a focal spot of 5-10 μm .

5

6 It is therefore an object of the invention to provide
7 an apparatus for carrying out X-ray fluorescence
8 spectrometry which is portable yet which is capable
9 of analysing samples of are less than 30 μm .

10

11 According to a first aspect of the present invention
12 there is provided an apparatus for carrying out X-ray
13 fluorescence spectrometry comprising an X-ray
14 generating tube and two paraboloidal X-ray reflecting
15 mirrors, the generating tube having an X-ray source
16 and an X-ray exit window through which X-ray
17 radiation from said source is emitted,
18 the first mirror being aligned on a first axis and
19 positioned in close coupled arrangement adjacent to
20 the exit window, the second mirror being aligned on
21 said first axis and being positioned in spaced apart
22 relationship to the first mirror,
23 the first mirror being adapted to collect diverging
24 X-ray radiation at its first end adjacent to the
25 collecting window and to emit X-ray radiation in a
26 substantially parallel beam at its second end,
27 the second mirror being adapted to collect
28 substantially parallel X-ray radiation at its first
29 end closest to the first mirror and to emit X-ray
30 radiation in a focused beam at its second end.

31

1 By using first and second mirrors in this way, the
2 focal spot on the target of the X-ray tube is
3 transferred to the image plane, at unity
4 magnification. The focal spot at the image plane on
5 the sample subjected to fluorescence has a high
6 brightness, and focal spots on the sample of diameter
7 less than 15 µm are possible.

8

9 Preferably the first and second mirrors are
10 cylindrical specularly reflecting mirrors.
11 Preferably the first end of the first mirror is
12 positioned between 5 and 50 mm from the X-ray source.

13

14 Preferably the apparatus further comprises a housing
15 containing the first and second mirrors.

16

17 The second mirror may be fixed in position relative
18 to the first mirror.

19

20 Alternatively the second mirror may be movable in
21 position relative to the first mirror. The apparatus
22 may further comprise a guide means for guiding said
23 second mirror in a direction parallel to the first
24 axis, and adjustment means for adjusting the spacing
25 of the first and second mirrors.

26

27 The apparatus may further comprise angular adjustment
28 means adapted to allow angular adjustment of the
29 mirror housing with the X-ray generator tube.

30

1 Preferably the X-ray generator tube is adapted to
2 produce an X-ray source at the target having a
3 maximum width of less than 50 µm, more preferably
4 less than 15 µm.

5

6 According to a second aspect of the present invention
7 there is provided a method of delivering X-ray
8 radiation to a specimen for the purpose of X-ray
9 fluorescence spectrometry using an X-ray generating
10 tube, the generating tube having an X-ray exit window
11 through which X-ray radiation is emitted,
12 the method comprising placing first and second
13 paraboloidal X-ray reflecting mirrors between the
14 exit window and the specimen,
15 using the first mirror to collect diverging X-ray
16 radiation at its first end adjacent to the exit
17 window and to emit X-ray radiation in a substantially
18 parallel beam at its second end,
19 and using the second mirror to collect substantially
20 parallel X-ray radiation at its first end closest to
21 the first mirror and to emit X-ray radiation at its
22 second end to a focused spot on the specimen.

23

24 Preferably the method uses an apparatus according to
25 the first aspect of the invention.

26

27 Embodiments of the invention will now be described,
28 by way of example only, with reference to the
29 accompanying figures, where:

30

1 Fig. 1 is a schematic view of two X-ray focusing
2 mirrors used in accordance with the invention to
3 focus an X-ray beam from the source on the X-ray
4 target to the sample to be subject to X-ray
5 fluorescence spectrometry;

6

7 Fig. 2 is a schematic view of an apparatus according
8 to a first aspect of the invention having mirrors
9 fixed relative to each other; and

10

11 Fig. 3 is a schematic view of an apparatus according
12 to a second aspect of the invention having mirrors
13 adjustable relative to each other.

14

15 Referring to Fig. 1 there is shown, in a schematic
16 form and not to scale, an X-ray generating tube 1
17 having an exit window 3, an electron source 6, an
18 anode 7, focusing and stigmator coils 8 and a target
19 2 on which is formed an X-ray source 9. A suitable
20 X-ray generating tube is the MICRO SOURCE™ tube
21 described in International Patent Application No
22 PCT/GB97/02022, which is a compact X-ray generator
23 capable of producing small-size, high intensity X-ray
24 sources for low power input. Typically the exit
25 window 3 of the generator 1 is provided in the narrow
26 portion 4 of the X-ray tube about which the X-ray
27 focusing coils 8 are arranged, to the side of the X-
28 ray target 2. A first X-ray focusing mirror 11, the
29 collection mirror, is positioned adjacent to the exit
30 window 3 in close coupled arrangement, and a second
31 X-ray focusing mirror 12, the focusing mirror, is

1 arranged coaxially with the first X-ray focusing
2 mirror 11, to transfer the . Suitable mirrors 11, 12
3 are MICROMIRROR™ X-ray optics as supplied by Bede
4 Scientific Instruments Ltd. The mirrors are
5 cylindrical specularly reflecting mirrors. Each
6 mirror comprises a cylindrical body having an axially
7 symmetrical passage extending therethrough. There is
8 an aperture at each end of the body which
9 communicates with the passage. The reflecting
10 surface is on the inside of the long axis of the
11 cylinder and has a shape corresponding to a
12 paraboloid of revolution about the long axis of the
13 cylinder.

14

15 A paraboloidal profile produces an almost parallel,
16 essentially non-divergent beam 14. The interior
17 reflecting surface 16 is coated in an exceptionally
18 smooth coating of gold or similar in order to provide
19 specular reflectivity. Typically the mirror is made
20 of nickel and is of the order of 10 to 100 mm in
21 length, typically about 30 mm. The outside diameter
22 of the mirror is typically 6 mm. The internal
23 diameter is typically less than 4 mm. The entry
24 aperture is generally smaller than the exit aperture.

25

26 The two mirrors have an identical profile. The
27 source to first mirror distance is in the range 5 to
28 50 mm.

29

1 Typically the X-ray generator produces a sub-15 μm
2 spot source on a target of less than 10 mm diameter
3 at a power of up to 30 W.

4

5 The first mirror or paraboloidal optic 11 has a high
6 angle of collection and reflects X-rays into a
7 substantially parallel beam. In practice a beam of
8 divergence less than 40 arc seconds can be achieved.

9

10 The second mirror or paraboloidal optic 12 takes the
11 parallel beam and focuses it down to a spot 15 on the
12 specimen 20 of a size similar to that of the X-ray
13 source, typically a spot with a diameter of less than
14 15 μm .

15

16 The focus 15 of the second optic 12 is typically
17 about 10 to 20 mm away from the far end 13 of optic,
18 giving a much more convenient working distance than
19 is available from prior art XRF apparatus, such as
20 monocapillaries.

21

22 The distance between the two optics 11, 12 may be
23 continuously changed without affecting the focal spot
24 quality, thereby allowing a range of source to sample
25 distances X to be achieved. Typically distance X
26 will be 100 mm or more.

27

28 X-ray optics have very well defined profiles and low
29 surface roughness, and therefore work at very high
30 efficiency. By using paraboloidal mirrors the
31 apparatus of the invention achieves broad band

1 transmission of X-rays, with an efficiency close to
2 1, since only double reflection of the X-ray
3 radiation is required.

4

5 The invention achieves high X-ray brightness at the
6 focal plane on the target, with a focal spot diameter
7 of as low as 10 µm.

8

9 The apparatus of the invention is truly portable,
10 giving it applications in areas such as forgery
11 detection, which require the apparatus to be taken to
12 the specimen.

13

14 A parabolic surface will produce a parallel beam if
15 the source is placed at the focal point. Conversely
16 a focused beam will be brought to a focus when a
17 parabolic surface is illuminated with a parallel
18 beam. Therefore the method and apparatus of the
19 invention serves to transfer the image of the X-ray
20 spot from the target to the specimen. It should be
21 noted that the target may not be perpendicular to the
22 axis of the of the mirrors, so that the effective
23 dimension of the image on the target, when viewed
24 along the axis of the mirrors, is less than the
25 actual dimension on the target.

26

27 The focal spot size at the specimen is thus primarily
28 determined by the spot size on the target of the X-
29 ray tube. Since the first mirror produces a parallel
30 beam, the focal spot size at the specimen is, within
31 practical limits, independent of the distance of the

1 second mirror along the beam axis. Therefore the
2 second mirror can be placed at the required distance
3 from the first in order to suit the geometrical
4 requirements of the equipment.

5

6 Figs. 2 and 3 show two schematic arrangements for
7 housing the apparatus of the invention.

8

9 In the simplest case, shown in Fig. 2, the collector
10 and focusing mirrors 11, 12 are aligned with each
11 other and are fixed within a cylindrical housing 30.
12 The housing is aligned relative to the X-ray source
13 9, shown purely schematically in Figs. 2 and 3, on
14 the beam axis 32, either fixedly or adjustably. The
15 housing 30 may be subject to a partial or total
16 vacuum, to improve the efficiency of the mirrors and
17 reduce energy absorption as the X-rays pass through
18 the gas in the housing 30. It is to be understood
19 that in practice the source 9 is part of an X-ray
20 generating tube 1 (not shown in Figs. 2 and 3).

21

22 In use the housing 30 is placed adjacent to the X-ray
23 source, and a control mechanism 35 allows fine
24 adjustment of the position of the housing 30 in the
25 x, y and z directions so that the axis 32 of the
26 mirrors is accurately aligned with the X-ray source 9
27 and directed to the specimen 20. The control
28 mechanism 35 may comprise any suitable mechanisms
29 which permit fine translational adjustment, such as
30 lead screws or Vernier controls.

31

1 In the example of Fig. 3, each mirror 11, 12 is
2 provided with a separate housing 40, 41. The
3 housings 40, 41 may further be contained in an outer
4 housing, not shown, which may be partially or
5 completely evacuated. The apparatus allows alignment
6 of the second mirror 12 relative to the first mirror
7 11 and translation of the second mirror 12 along the
8 beam axis 43 by means of control mechanism 44.

9

10 Alignment of the whole mirror assembly relative to
11 the X-ray source 9 is possible by means of control
12 mechanism 45. Mechanisms 44 and 45 are similar to
13 mechanism 35 described with reference to Fig. 2, and
14 are not described further.

15

16 Although the invention has been described with
17 reference to a microfocus X-ray generator, the
18 invention can be used with any suitable X-ray
19 generator which is capable of producing a small
20 source of sufficient intensity.

21

22 The mirror housing 30, 40 may be attached to the X-
23 ray tube 1 or may be positioned independently.

24

25 These and other modifications and improvements can be
26 incorporated without departing from the scope of the
27 invention.

1 CLAIMS

2

3 1. An apparatus for carrying out X-ray fluorescence
4 spectrometry comprising an X-ray generating tube (1) and
5 two paraboloidal X-ray reflecting mirrors (11, 12), the
6 generating tube having an X-ray source (9) and an X-ray
7 exit window (3) through which X-ray radiation from said
8 source is emitted,

9 the first mirror (11) being aligned on a first axis (32,
10 43) and positioned in close coupled arrangement adjacent
11 to the exit window (3), the second mirror (12) being
12 aligned on said first axis and being positioned in spaced
13 apart relationship to the first mirror (11),

14 the first mirror (11) being adapted to collect diverging
15 X-ray radiation at its first end adjacent to the
16 collecting window (3) and to emit X-ray radiation in a
17 substantially parallel beam at its second end,

18 the second mirror (12) being adapted to collect
19 substantially parallel X-ray radiation at its first end
20 closest to the first mirror and to emit X-ray radiation
21 in a focused beam at its second end.

22

23 2. An apparatus according to Claim 1, wherein the first
24 and second mirrors (11, 12) are cylindrical specularly
25 reflecting mirrors.

26

27 3. An apparatus according to Claim 1 or 2, wherein the
28 first end of the first mirror (11) is positioned between
29 5 and 50 mm from the X-ray source (9).

30

31 4. An apparatus according to any preceding Claim,
32 wherein the apparatus further comprises a housing
33 containing the first and second mirrors.

1

2 5. An apparatus according to any preceding Claim,
3 wherein the second mirror is fixed in position relative
4 to the first mirror.

5

6 6. An apparatus according to any of Claims 1 to 4,
7 wherein the second mirror is movable in position relative
8 to the first mirror.

9

10 7. An apparatus according to Claim 6, further
11 comprising a guide means for guiding said second mirror
12 in a direction parallel to the first axis, and adjustment
13 means for adjusting the spacing of the first and second
14 mirrors.

15

16 8. An apparatus according to any preceding Claim,
17 further comprising angular adjustment means adapted to
18 allow angular adjustment of the mirror housing with the
19 X-ray generator tube.

20

21 9. An apparatus according to any preceding Claim,
22 wherein the X-ray generator tube is adapted to produce an
23 X-ray source at the target having a maximum width of less
24 than 50 µm, more preferably less than 15 µm.

25

26 10. An apparatus according to any preceding Claim,
27 wherein the apparatus is portable and the X-ray generator
28 is a microfocus generator.

29

30 11. A method of delivering X-ray radiation to a specimen
31 for the purpose of X-ray fluorescence spectrometry using
32 an X-ray generating tube, the generating tube having an

1 X-ray exit window through which X-ray radiation is
2 emitted,
3 the method comprising placing first and second
4 paraboloidal X-ray reflecting mirrors between the exit
5 window and the specimen,
6 using the first mirror to collect diverging X-ray
7 radiation at its first end adjacent to the exit window
8 and to emit X-ray radiation in a substantially parallel
9 beam at its second end,
10 and using the second mirror to collect substantially
11 parallel X-ray radiation at its first end closest to the
12 first mirror and to emit X-ray radiation at its second
13 end to a focused spot on the specimen.

14

15 12. A method according to Claim 11, wherein the first
16 and second mirrors (11, 12) are cylindrical specularly
17 reflecting mirrors.

18

19 13. A method according to Claim 11 or 12, wherein the
20 first end of the first mirror (11) is positioned between
21 5 and 50 mm from the X-ray source (9).

22

23 14. A method according to any one of Claims 11 to 13,
24 wherein the focused spot on the specimen has a maximum
25 dimension of 50 μm .

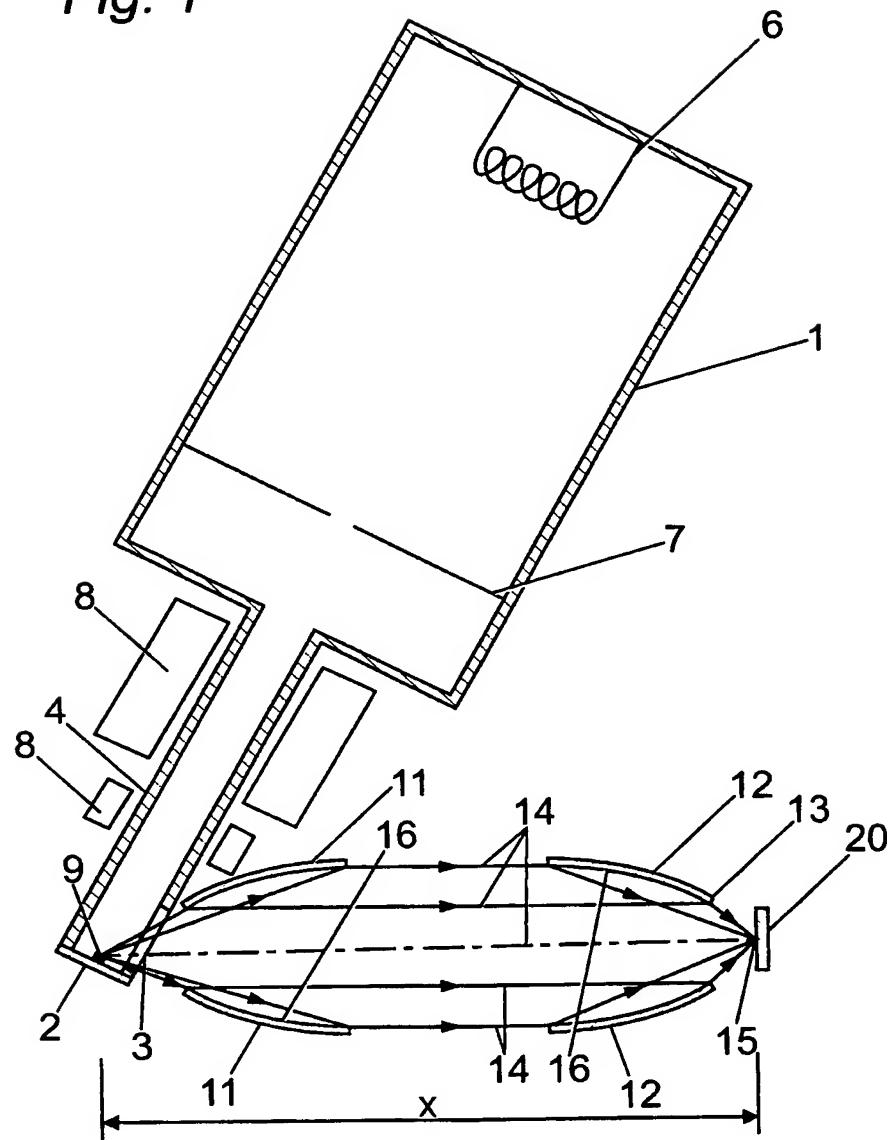
26

27 15. A method according to any one of Claims 11 to 14,
28 further comprising the step of adjusting the spacing of
29 the first and second mirrors to produce a focused spot on
30 the specimen.

31

32 16. A method according to any one of Claims 11 to 15,
33 wherein the X-ray generator is a microfocus generator.

1 / 2

Fig. 1

2 / 2

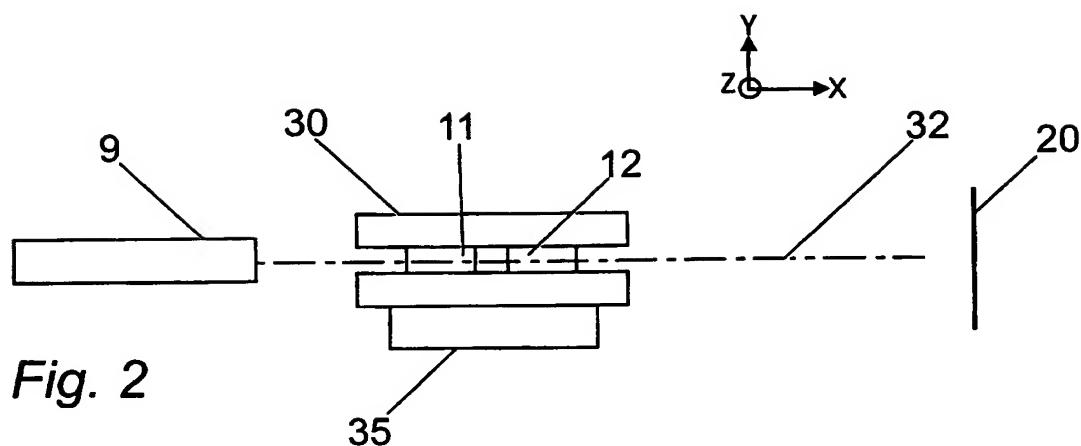


Fig. 2

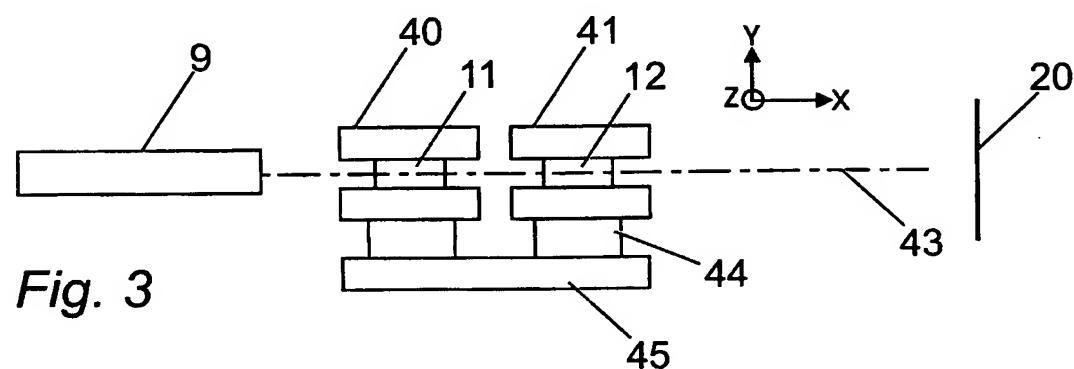


Fig. 3